B.Sc. Semester-IV
Core Course-IX (CC-IX)
Organic Chemistry-III

I. Nitrogen Containing Functional Groups

2. Amines: Nomenclature and Physical Properties

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I Nitrogen Containing Functional Groups

Preparation and important reactions of nitro and compounds, nitriles and isonitriles Amines: Effect of substituent and solvent on basicity; Preparation and properties: Gabriel phthalimide synthesis, Carbylamine reaction, Mannich reaction, Hoffmann's exhaustive methylation, Hofmann-elimination reaction; Distinction between 1°, 2° and 3° amines with Hinsberg reagent and nitrous acid.

Coverage:

1. Amines: Nomenclature, Physical Properties, Some Interesting and Useful Amines

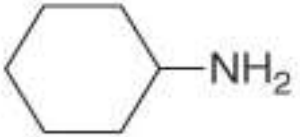
Amines

Nomenclature

- **1^0 Amines are named using either systematic or common names.**
- **To assign a systematic name, find the longest continuous chain bonded to the amine nitrogen, and change the *–e* ending of the parent alkane to the suffix *–amine*. Then use the usual rules of nomenclature to number the chain and name the substituents.**
- **To assign a common name, name the alkyl group bonded to the nitrogen atom and add the word amine, forming a single word.**

Examples

Systematic name: **methanamine**
Common name: **methylamine**

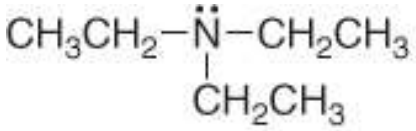


Systematic name: **cyclohexanamine**
Common name: **cyclohexylamine**

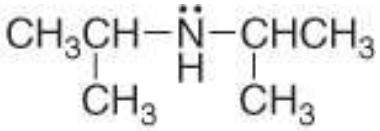
Amines

Nomenclature

- **Secondary and 3^0 Amines having identical alkyl groups are named using the prefix di- or tri- with the name of the primary amine.**



triethylamine

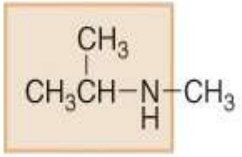


diisopropylamine

- **Secondary and 3^0 Amines having more than one kind of alkyl group are named as *N*-substituted primary amines using the following procedure:**

Example Name the following 2° amine: $(CH_3)_2CHNHCH_3$.

Step [1] Designate the longest alkyl chain (or largest ring) bonded to the N atom as the parent amine and assign a common or systematic name.

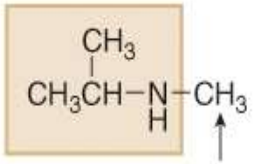


3 C's in the longest chain → isopropylamine (common name) or 2-propanamine (systematic name)

Amines

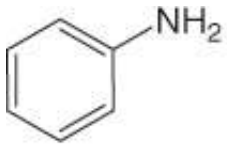
Nomenclature

Step [2] Name the other groups on the N atom as alkyl groups, alphabetize the names, and put the prefix *N*- before the name.

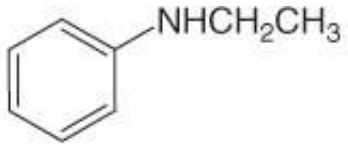


Answer: ***N*-methylisopropylamine (common name)**
or
***N*-methyl-2-propanamine (systematic name)**

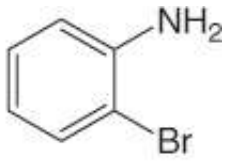
- **Aromatic amines are named as derivatives of aniline.**



aniline

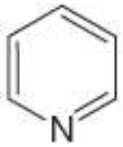


N-ethylaniline



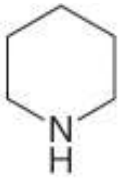
o-bromoaniline

- **There are many different nitrogen heterocycles, each with a different name. The N atom is considered to be at position "1".**

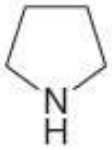


pyridine

pyrrole



piperidine

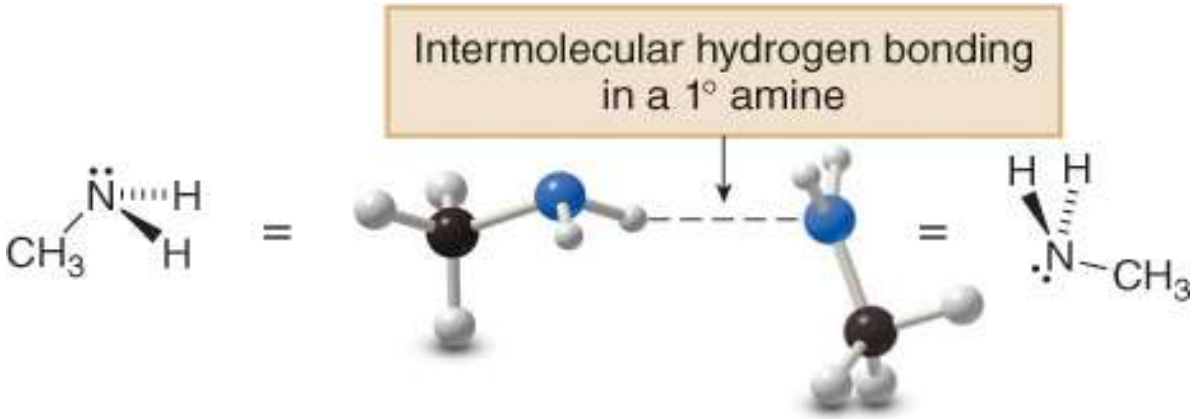


pyrrolidine

Amines

Physical Properties

- **Amines exhibit dipole-dipole interactions because of the polar C—N and N—H bonds.**
- **Primary and 2^0 amines are capable of intermolecular hydrogen bonding because they contain N—H bonds.**
- **Since nitrogen is less electronegative than oxygen, these hydrogen bonds are weaker than those between O and H.**



Amines

Physical Properties of Amines

Property	Observation
Boiling point and melting point	• Primary (1°) and 2° amines have higher bp's than similar compounds (like ethers) incapable of hydrogen bonding, but lower bp's than alcohols that have stronger intermolecular hydrogen bonds. $CH_3CH_2OCH_2CH_3$ MW = 74, bp 38 °C $CH_3CH_2CH_2CH_2NH_2$ MW = 73, bp 78 °C $CH_3CH_2CH_2CH_2OH$ MW = 74, bp 117 °C **Increasing intermolecular forces** **Increasing boiling point** • Tertiary (3°) amines have lower boiling points than 1° and 2° amines of comparable molecular weight, because they have no N–H bonds and are incapable of hydrogen bonding. 3° amine: $CH_3CH_2N(CH_3)_2$ MW = 73, bp 38 °C, **no N–H bond** $CH_3CH_2-\underset{H}{N}-CH_2CH_3$ (2° amine, higher bp) MW = 73, bp 56 °C, **N–H bond**
Solubility	• Amines are soluble in organic solvents regardless of size. • All amines having ≤ 5 C's are H_2O soluble because they can hydrogen bond with H_2O (Section 3.5C). • Amines having > 5 C's are H_2O insoluble because the nonpolar alkyl portion is too large to dissolve in the polar H_2O solvent.

MW = molecular weight

Amines

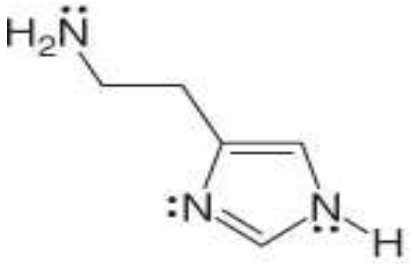
Some Interesting and Useful Amines

- **Many low molecular weight amines have foul odors.**
- **Trimethylamine [$(CH_3)_3N$], formed when enzymes break down certain fish proteins, has the characteristic odor of rotting fish.**
- **Putrescine ($NH_2CH_2CH_2CH_2CH_2NH_2$) and cadaverine ($NH_2CH_2CH_2CH_2CH_2CH_2NH_2$) are both poisonous diamines with putrid odors. They too are present in rotting fish, and are partly responsible for the odors of semen, urine, and bad breath.**
- **Naturally occurring amines derived from plant sources are called alkaloids.**

Amines

Some Interesting and Useful Amines

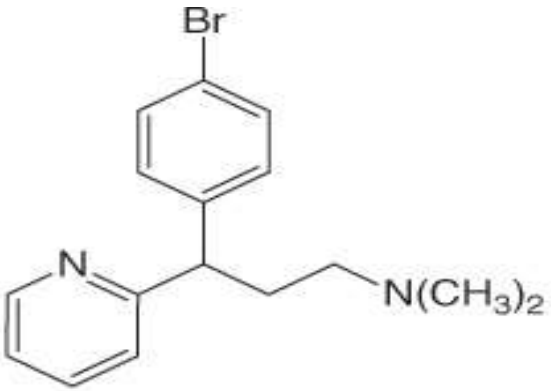
- **Histamine, a rather simple triamine that is present in many tissues, is responsible for a wide variety of physiological effects.**



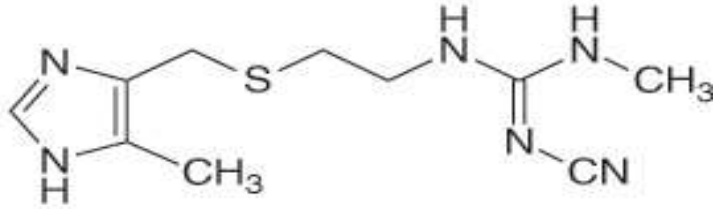
histamine

- **Understanding the physiological properties of histamine has helped chemists design drugs to**

counteract some of its undesirable effects. Antihistamines bind to the same active site as histamine in the cell, but they evoke a different response. Examples are brompheniramine and cimetidine.



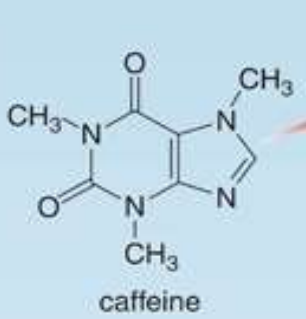
brompheniramine
antihistamine in several
over-the-counter allergy remedies



cimetidine
(Tagamet)
antiulcer drug

Amines

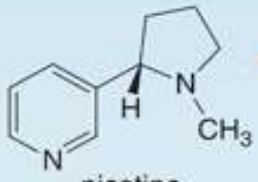
Some Interesting and Useful Amines



caffeine

coffee

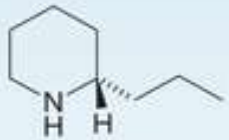
- **Caffeine** is a bitter alkaloid found in coffee, tea, cola beverages, and chocolate. Caffeine is a mild stimulant, usually imparting a feeling of alertness after consumption. It also increases heart rate, dilates airways, and stimulates the secretion of stomach acid. Excessive use can result in insomnia.



nicotine

tobacco

- **Nicotine** is an addictive and highly toxic compound isolated from tobacco. In small doses it acts as a stimulant, but in large doses it causes depression, nausea, and even death. Nicotine is synthesized in plants as a defense against insect predators, and is used commercially as an insecticide.



coniine

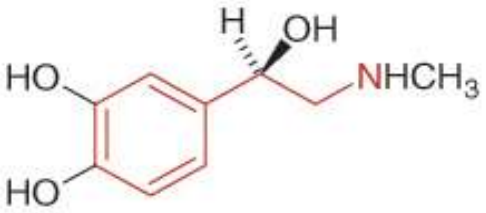
hemlock

- **Coniine**, a poisonous alkaloid isolated from the seeds, leaves, and roots of hemlock (*Conium maculatum*), has been known since ancient times. Ingestion causes weakness, paralysis, and finally death. The Greek philosopher Socrates was executed by being forced to drink a potion prepared from hemlock in 339 B.C.

Amines

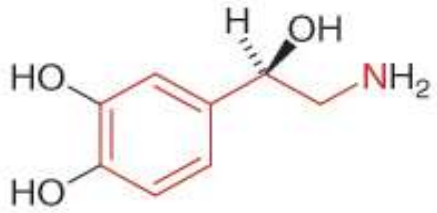
Some Interesting and Useful Amines

- **A large number of physiologically active compounds are derived from 2-phenethylamine ($C_6H_5CH_2CH_2NH_2$). These compounds include adrenaline, noradrenaline, methamphetamine, and mescaline. Each contains a benzene ring bonded to a two-carbon unit with a nitrogen atom (shown in red).**



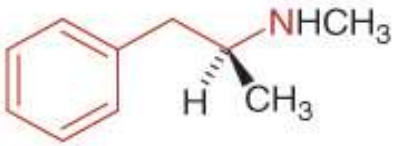
adrenaline
(epinephrine)

a hormone secreted in response to stress
(Chapter 7, introductory molecule)



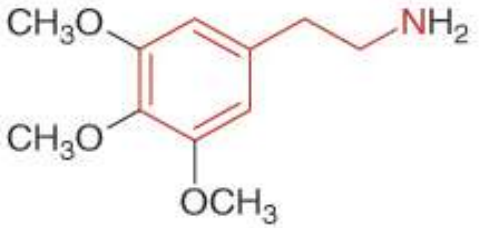
noradrenaline
(norepinephrine)

a neurotransmitter that increases heart rate
and dilates air passages



methamphetamine

an addictive stimulant sold as
speed, meth, or crystal meth



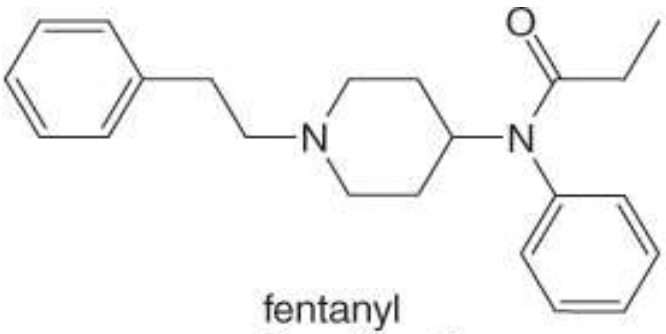
mescaline

a hallucinogen isolated from peyote, a cactus native
to the southwestern United States and Mexico

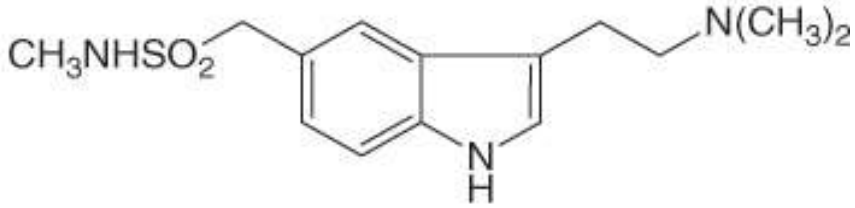
Amines

Some Interesting and Useful Amines

- **Cocaine, amphetamines, and several other addicting drugs increase the level of dopamine in the brain, which results in a pleasurable "high." With time, the brain adapts to increased dopamine levels, so more drug is required to produce the same sensation.**
- **Understanding the neurochemistry of these compounds has led to the synthesis and availability of several useful drugs. Examples are fentanyl and sumatripan.**

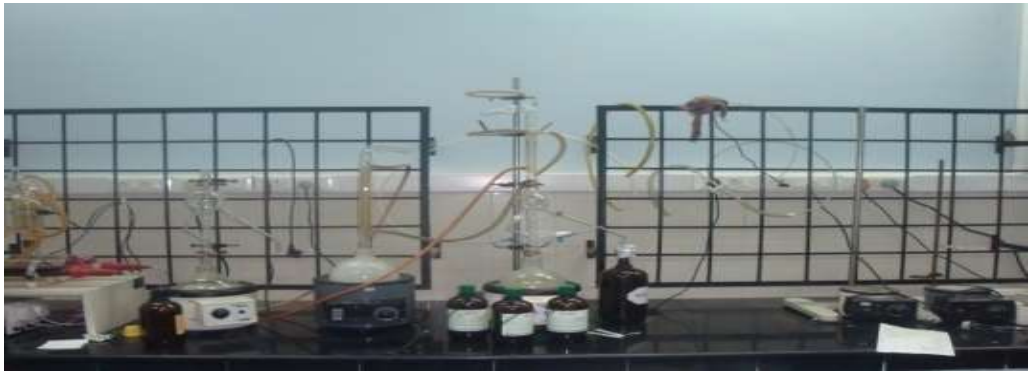


fentanyl
a narcotic pain reliever



sumatriptan
Trade name: Imitrex

Thank You



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